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In conclusion, a senes of experiments has been performed to optimize the growth conditions for GaN nanowtres. A systematic study of the effects of growth parameters on the shape and size of crystal products reveals important infoniiation. A growth map with a wider rangc of experimental parameters can thus be proposed. The map has three distinct zones. The shape and the size of the products in every zone dcpcnd on temperature, NH3 flow rate and GaN crystal structurc, if the growth time is fixed to be thee hours. An effective surface diffusion length comprises Ca surface diffusion length and the anisotropy of the Ga surface diffusion length. An striking feature of the investigation is that, if the growth rate is introduced into a growth model all observed results can be successfully explained. The optimal growth parameters have been determined. One remarkable observation is the formation of nanowires with uniform diameter, of clear crystal structure, and of length larger than 1 mm. For them, the location distribution is uniform and the yield is quite high. The growth map, develoed for the first time, to our knowledge, gives a clear direction of how to accomplish nano- or micro products in 1-, 2-, and 3D. It is indeed exciting.

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Nanowires are very promising as elemental building blocks for nanotechnology applications 1-5]. Among them, GaN nanowires exhibit large energy bandgaps and structural confinement which are useful for realizing nanosized ultraviolet or blue emitters, detectors, high-speed field-effect transistors, and high-temperature microelectronic devices [6,7]. However, these electronic and optical properties strongly depend on size and geometry. Surface effects also become important in thinner nanowires. GaN nanowires synthesized so far have lengths ranging from several micrometers and diameters ranging from 10 to 50 nm. GaN nanowires can provide the opportunity also to theoretically study the quantum effects in one dimension, and to verify them experimentally [8]. During the past years, GaN nanowires have been synthesized by employing several different approaches, including arc-discharge, laser-assisted catalytic growth, direct reaction of the mixture, hot filament chemical vapor deposition [9], etc. For example, high-quality GaN nanowires have been synthesized using a Ni catalyst by direct reaction of the mixture of Ga metal and GaN powder with flowing NH_3 at about 1000 °C and using thermal chemical vapor deposition method. In the oxide assisted method, oxides play a central role in the nucleation and growth of nanowires via a series of oxidation-reduction processes.

There are two reasons fascinating our interests in systematically studying the nanowire growth, in trying to extend the size of these nanowires from nano to micro range, and in modifying the dimension from 1 dimension, 1D, (wire or rod) to 2 dimension, 2D (platelet, but not films), to 3 dimension, 3D (e.g. grain). As indicated earlier, free-standing materials with different sizes (e.g., nano-, meso-, micro sizes) and shapes (e.g., 1-, 2-, 3D shapes) have various applications in electronic and opto-electronic devices. For example, W wires and Carbon tubes can be used as STM or AFM tips [13,14], gold wires can be used as connecting wires of single electron devices, and micro rods can be used as parts of nano-micro-robots [15]. There are special properties and applications of nano-micro particles because of their size effects [16,17]. Single crystal grain can be used as seeds for growing bulk crystal.

Our growth method, which involves the direct reaction of Ga with NH_3 without the application of a template [18] and a catalyst [19], is different from previous approaches. It has the ability to grow various materials, including elements, compounds, and alloys of desired shape and size. Primary investigations reveal that a systematic and detailed study of nanowires grown under various conditions is very important for the following reasons: First, for GaN nanowires, the optimal growth conditions can be found for certain given shapes and sizes. These optimal conditions are indeed exciting: the growth of nanowires of uniform size and single-crystal structure and of length longer than 1 mm can be accomplished. Second, the conditions provide us with significant knowledge of the details of the growth method. For example, it suggests to which degree the size, shape, composition and structure of materials can be controlled using this growth method, and how to grow various materials. Third, because this growth method doesn't use any template or catalyst, it has potential to be extended to grow other kinds of materials, such as group III-V binaries (InAs, InN, already grown in our lab), group II-VI binaries (ZnO), and elements (Cu, Si, Al). Fourth, knowledge of two dimensional material structures such as micro films, surfaces, and interfaces is quite rich. However, such a knowledge of materials with nano-, meso-, and micro-size and of 1-, 2-, and 3D shape is very limited. Some new phenomena and concepts dictating the growth in this growth range should be very promising. Materials parameters, such as effective diffusion length, mutual restriction of maximum size under different growth directions, maximum single crystal face area over which single crystal growth stops, and the final product obtained by employing the said growth method might be in 1D with any long.

The details of the growth technique employed to synthesize the GaN nano/micro structures can be found in Refs. [10-11]. About 3 gm of pure Ga metal was put on a BN boat placed in a quartz liner, about 150 mm in length and 20 mm in outer diameter (OD). This, in turn, was fitted inside another larger quartz tube, called the process chamber, having 25 mm outer diameter. The liner, as shown schematically in Fig. 1, served two purposes : first it protected the process chamber from being contaminated by impurities, and second, it provided the surface upon which the GaN nano/micro

structures could be formed. The process chamber was mechanically pumped down to a pressure of 30 mTorr. At the beginning of the growth process, pure NH_3 was passed into the system via a mass-flow controller. The process chamber was heated using a 3-zone furnace for a period of 3 hours during the experiment.

A series of experiments were performed to determine the three controllable parameters of the experiment : NH_3 flow rate, growth temperature and chamber pressure. These were manipulated by changing one parameter while keeping the other two parameters constant. NH_3 flow rate was changed from 20 sccm to 150 sccm, the growth temperature was increased from 825 °C to 1100 °C, and the chamber pressure was increased from 2 Torr to 100 Torr. GaN nano/micro structures, formed on the BN boat and on the inner wall of the liner, are shown as dotted line in Fig. 1. Samples were collected for measurements. The composition, size and structure of the samples were studied by using optical microscope, scanning electron microscope (SEM) and the energy dispersive X-Ray spectroscope (EDS).

Analyzing the products grown on the inside surface of the liner at 900 °C and 15 Torr it was revealed that there was a distribution of two distinct and easily separable products, viz., single crystal nano/meso wires and single crystal hexagonal micro platelets. The distribution exhibited essentially the same characteristics even when the NH_3 flow rate differed (60-150 sccm). Near the end of the liner, where NH_3 was introduced 'upstream,' there was a high density of wires, but no platelets at all. Moving further down the stream, it was found that the density of the wires began to diminish, and the platelets tended to emerge as the prominent product, particularly, near the end where NH_3 exited 'down stream.

Varying the chamber pressure between 2 and 100 Torr, and keeping the NH_3 flow rate at 100 sccm and temperature at 900 °C, had a dramatic effect on the outcome of the experiment. The results corresponding to 2 Torr, 5 Torr, 15 Torr, 50 Torr, and 100 Torr, respectively, and formed on the walls of the liner, could be divided into 5 distinct categories. At a pressure of 2 Torr, the observed GaN nanowires had high density, which were observed mainly near the entrance (on the left hand

side) of the liner. The density of the nanowires decreased gradually as one moved towards the exit. In this area, the material was primarily polycrystalline GaN platelets formed on the wall of the liner; only polycrystalline GaN platelets were observed on the right hand end of the BN boat. At a pressure of 5 Torr, GaN nanowires formed on the walls of the liner, as well as on the BN boat, had, however, quite high density. The nanowire density along the liner was quite uniform, and very few GaN platelets were observed on the right of the GaN boat.

The products formed on the wall of the liner at pressures of 15 Torr and 2 Torr had many interesting features. One notable difference between the two was, however, that the GaN platelets formed at a pressure of 15 Torr were single crystals, while those formed at a pressure of 2 Torr were polycrystalline. The distribution of products observed on the BN boat was the same as that on the wall of the tube. At 50 Torr, only partial wetting of the Ga metal placed on the BN boat took place. However, at 100 Torr, no wetting was at all observed. Thus, no crystal products could be found either on the BN boat or on the liner wall. This was attributed to the diminishing possibility of the nitridation reaction itself.

A series of experiments were conducted to study the effect of varying the NH_3 flow rate on the shape, size and density of the nanowires. Keeping the chamber pressure constant at 5 Torr and the temperature at 900 °C, the NH_3 flow rate was varied between 20 and 150 sccm. At a pressure of 20 sccm, only shiny Ga metal was detected (see Fig 3(a)). As the ammonia flow rate was increased to 30 sccm, some polycrystalline platelets were also produced. These are shown in Fig. 3(b). As evident from Fig. 3(c), single crystal platelets with diameters of 20-40 μm began to appear at a flow rate of 30-50 sccm. This was a clear evidence of the preferential formation of big platelet at lower NH_3 flow rate. GaN nanowires started growing only when the pressure reached to about 50 sccm. There is a remarkable characteristic of these nanowires was that there was no obvious increase in their size for NH_3 flow rates higher than 80 sccm. The same series of experiments were conducted by setting the temperature to 1000 °C and 1100 °C, respectively. Essentially the same growth pattern, as observed for lower flow rate growth of GaN platelet, and for lower ammonia flow rate growth (but

much lower than that obtained at 900 °C) of nanowires, was confirmed. When we resorted to higher flow rate growth, micro rods were the dominant products at a temperature of about 1000 °C, and micro grains were the dominant products at a temperature of about 1100 °C.

A series of experiments were also carried out to study the effect of varying the temperature on the shapes and sizes of the GaN products. These shapes and sizes of the grown products were found to change considerably by varying the temperature between 875 and 1100 °C, but keeping the NH_3 flow rate constant at 100 sccm and the chamber pressure at 5 Torr. For temperature range between 875 and 900 °C, the main product was one dimensional GaN nano/micro wires. GaN wires grown at 900 °C with diameter of 80-130 nm. As the temperature was increased, the size increased, and the micro rods with diameter of 2-7 μm and length of 30-100 μm were produced at a temperature around 1000 °C. As the temperature was increased further to about 1100 °C, the growth of three dimensional micro grains set in . The size of these micro grains was about 50-100 μm.

In conclusion, a series of experiments has been performed to optimize the growth conditions for GaN nanowires. A systematic study of the effects of growth parameters on the shape and size of crystal products reveals important information. A growth map with a wider range of experimental parameters can thus be proposed. The map has three distinct zones. The shape and the size of the products in every zone depend on temperature, NH_3 flow rate and GaN crystal structure, if the growth time is fixed to be three hours. An effective surface diffusion length comprises Ga surface diffusion length and the anisotropy of the Ga surface diffusion length. An striking feature of the investigation is that, if the growth rate is introduced into a growth model all observed results can be successfully explained. The optimal growth parameters have been determined. One remarkable observation is the formation of nanowires with uniform diameter, of clear crystal structure, and of length larger than 1 mm. For them, the location distribution is uniform and the yield is quite high. All these are evident from Fig. 8. The growth map, develoed for the first time, to our knowledge,

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